BOEING

Engineering, Operations & Technology
Boeing Research & Technology

Comments on Cadmium Alternatives and Testing – IHE vs. EHE

ASTM F07.04 Hydrogen Embrittlement Workshop
November 17, 2011
Tampa, FL

Steve Gaydos
Technical Fellow – Boeing Research & Technology
ASTM F07 Chairman
ASTM F07.04 Subcommittee Chairman

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE **17 NOV 2011**	2. REPORT TYPE	3. DATES COVERED **00-00-2011 to 00-00-2011**

4. TITLE AND SUBTITLE **Comments on Cadmium Alternatives and Testing - IHE vs. EHE**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Boeing,P. O. Box 516,St. Louis,MO,63166**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Focused Workshop on Cadmium Plating Alternatives, August 30-31, 2011, Baltimore, MD. Sponsored by SERDP/ESTCP.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**29**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

ASTM F 2078 Terminology for IHE & EHE

internal hydrogen embrittlement (IHE)—hydrogen embrittlement caused by absorbed atomic hydrogen into the steel/metallic alloy from an industrial hydrogen emitting process coupled with stress, either residual or externally applied.

environmental hydrogen embrittlement (EHE)—hydrogen embrittlement caused by hydrogen introduced into a steel/ metallic alloy from an environmental source coupled with stress either residual or externally applied.

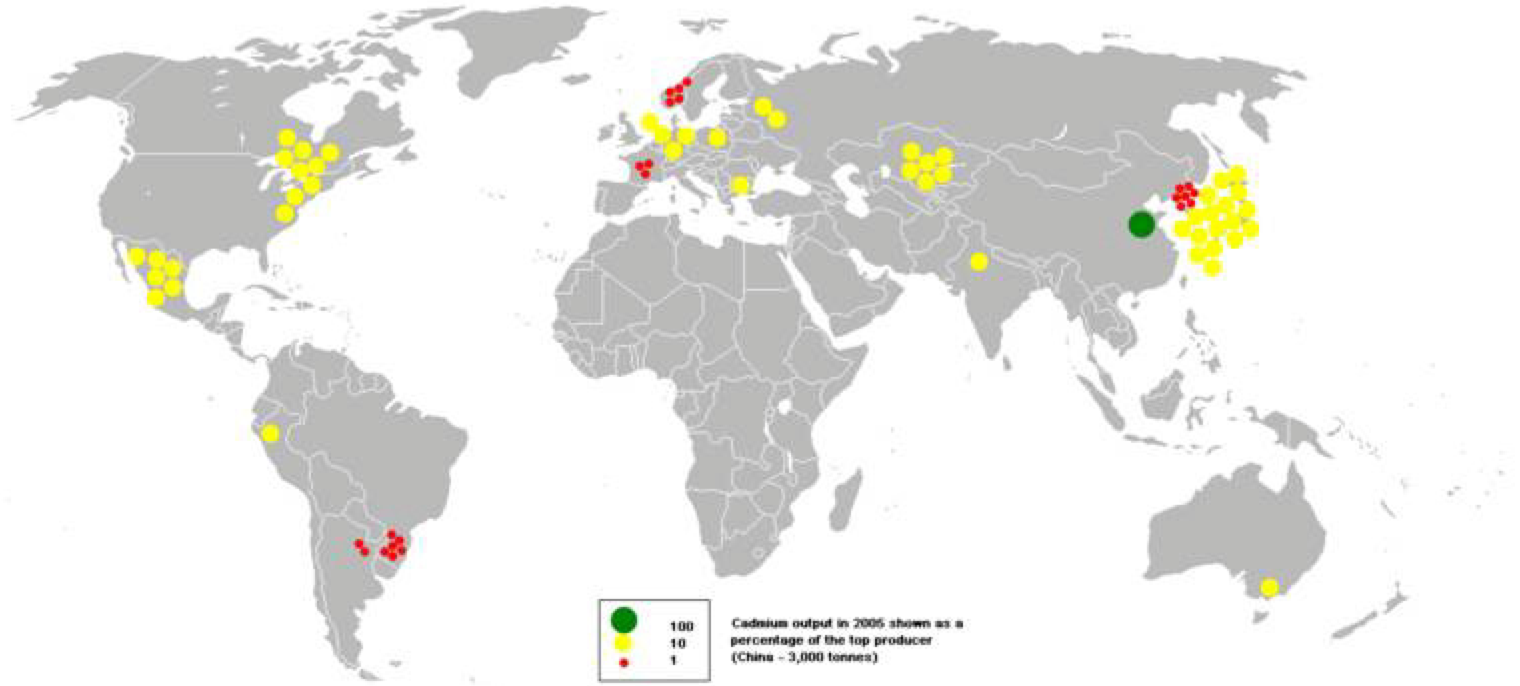
stress corrosion cracking (SCC)—a cracking process that requires the simultaneous action of a corrodent and sustained tensile stress.

Cadmium Properties - WikiFacts

- **Cadmium – Cd – Atomic No. 48 –**
  - **Oxidation State +2 – Sp. Gr. = 8.65**
- **Soft, blue-white metal melts at 610^{O} F**
  - Mohs Hardness 2 (Gypsum)
  - **Lubricous (Anti-Galling)**
- **Discovered in 1817**
  - **By – product of Zn Refining – Purified by Vacuum Distillation**
- **Corrosion Resistant in Salt Water**
  - **Better than Zn**
- **Good Electrical Properties**
  - **Solderable**
- **Cadmium has no known useful role in higher organisms.**
  - **Cadmium is an extremely toxic metal.**

Cadmium Production - WikiFacts

- **2009 – 18,800 metric tons Cd**
  - **China is Largest Producer of Cd**
    - **4,300 Tones/yr (or 9.4 million pounds)**



Cadmium Uses - WikiFacts

- **1930s – 40s**
  - **Coatings for Corrosion protection of Iron (62%)**
  - **Red, Yellow and Orange Pigments (26%)**
  - **Other uses (12%)**
- **Usage in coatings peaked in the 60s and 70s and then declined rapidly in the 80s and 90s (Env and Health Issues)**
- **Current use**
  - **Ni-Cd Batteries 81%**
  - **Coatings – 7%***
    - ***6 of the 7% Used by Aerospace**
  - **Pigments – 10%**
  - **Other Uses – 2%**

#1 Cd User in 2011

Why Are Cadmium Coatings So Good?

- **Provides Corrosion Protection to Steel - No red rust**
  - Corrosion Resistant Coating in Salt Water (Compared to Zinc)
    - Cd corrosion rate in salt water is lower than zinc
- **Sacrificially Protects Steel**
  - If Cd coating is scratched Cd coating will corrode first and prevent steel from corroding
- **Soft and Ductile**
  - Does Not Reduce the Fatigue Life of High Strength Steel (HSS)
  - Provides lubricous coating to fasteners and gears
    - Threads still require lubricant
- **Good Electrical Properties**
  - Low contact resistance
  - Cd oxides are conductive (as compared to aluminum oxides)
  - Solderable

Cadmium Issues

- **All forms of Cd (Cd^0 or Cd^{+2}) are Toxic**
  - Not like Cr Plating - Cr metal is non-toxic but Cr^{+6} is toxic
- **Do not use at > 450° F on HSS**
  - Causes Liquid / Solid Metal Embrittlement of HSS
- **Do not use in fuel tanks**
  - Reacts with Fuel
- **Do not use next to Ti**
  - Embrittles Ti
- **Poor corrosion performance in SO_2 salt spray (acidified)**
- **Plating Bath Contains Cyanides**
- **Causes Hydrogen Embrittlement Problems of HSS if not Properly Controlled**
  - Controlled by Plating Methods and Baking Plated Parts

Two Forms of Cadmium Plating Exist

ASTM F 519 Plating Conditions →

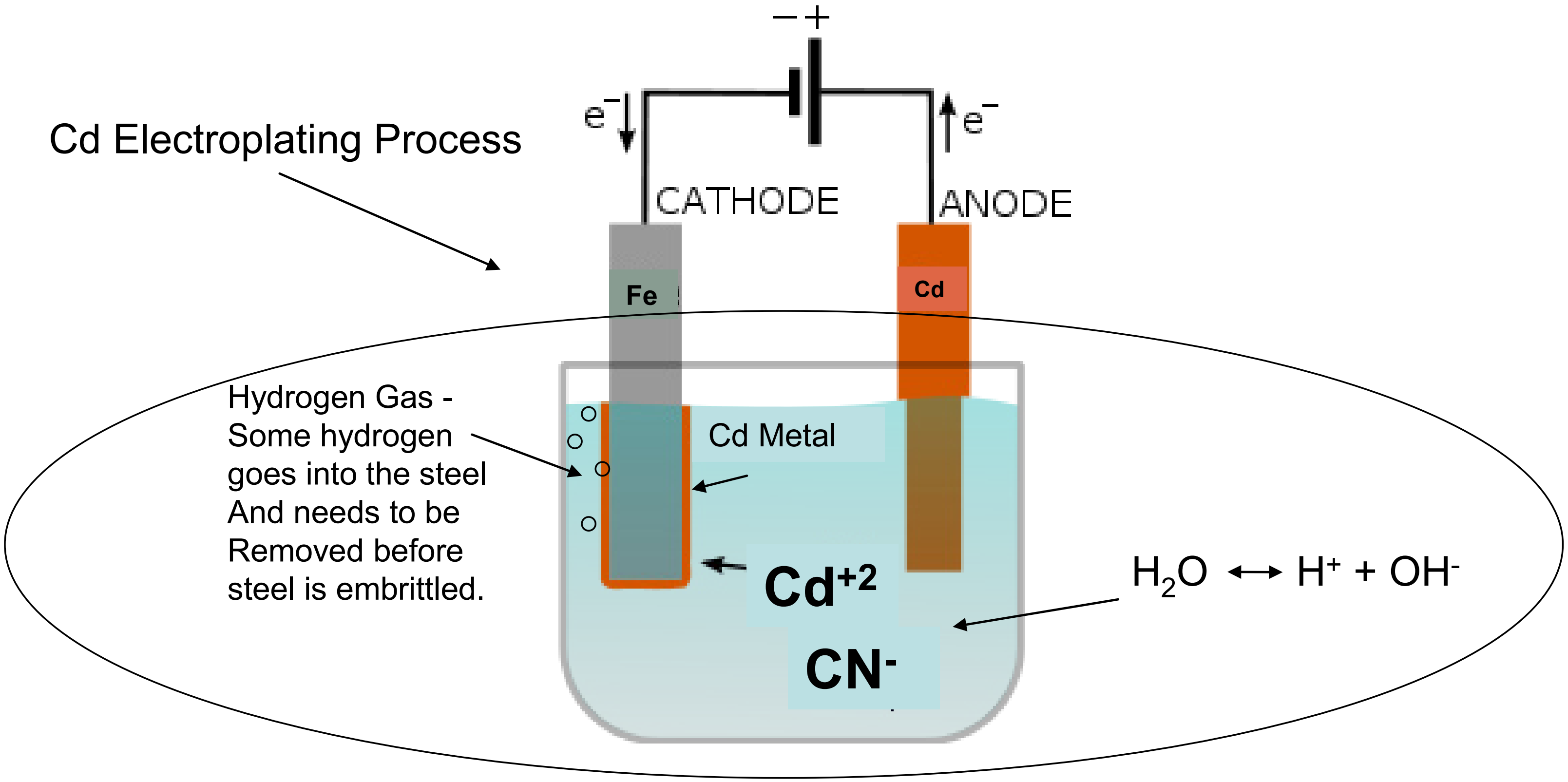
Treatment A
Bright Cadmium
AMS-QQ-P-416
Use on Steels < 180 ksi

or

Treatment B
Dull Cadmium
MIL-STD-870
Use on Steels > 180 ksi

Item	Treatment A		Treatment B
Bath composition:	Range	Optimum	
Cadmium (as CdO)	2.9 to 5.5 oz/gal (22 to 41 g/L)	4.5 oz/gal (33.7 g/L)	same as Treatment A
Total Sodium cyanide (NaCN)	12.0 to 16.0 oz/gal (89.9 to 120 g/L)	14 oz/gal (104 g/L)	same as Treatment A
Ratio NaCN to CdO	2.8/1 to 6.0/1	3.0/1	same as Treatment A
pH	12.0 or greater	12.0	same as Treatment A
Temperature	70–90°F (21–32°C)	75°F (24°C)	same as Treatment A
Sodium hydroxide (NaOH)[A]	1.0 to 3.2 oz/gal (7.5 to 24.0 g/L)	2.5 oz/gal (18.7 g/L)	same as Treatment A
Brightener such as ROHCO 20 X L or equivalent	Manufacturer's suggested range		None
Electroplating current	10 A/ft^2 (108 A/m^2)		60 A/ft^2 (645 A/m^2)
Electroplating time	30 minutes		6 minutes
Baking			
Baking temperature	375 ± 25°F (190 ± 14°C)		same as Treatment A
Baking time: Type 1 Specimen	Do Not Bake		23 h
Baking time: Type 2a Specimen	8 h		23 h
Chromate Treatment[B]	Yes		same as Treatment A

IHE – Cadmium Plating Process



Anode RXN: $Cd \rightarrow Cd^{+2} + 2e^-$

Cathode RXN #1: $Cd^{+2} + 2e^- \rightarrow Cd$

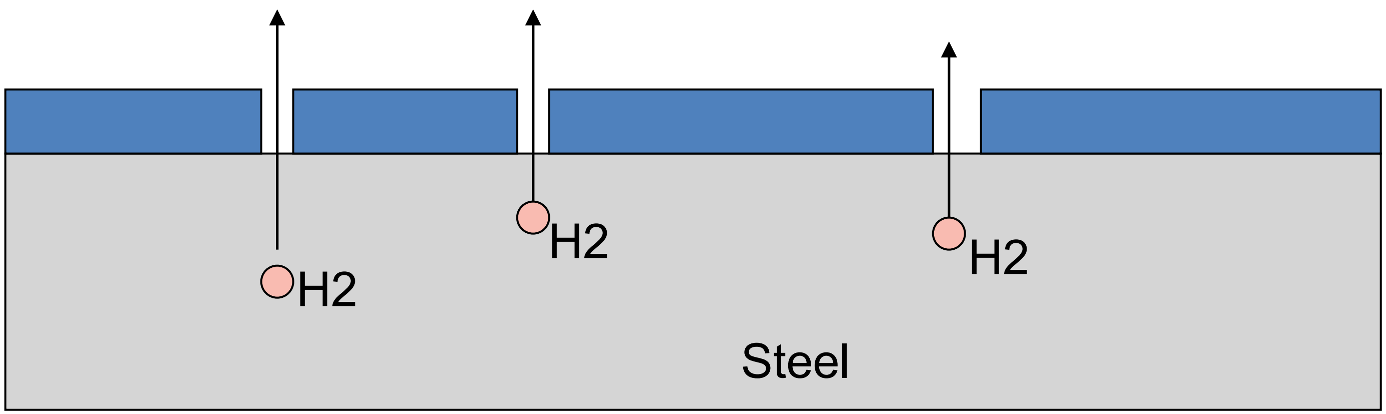
Cathode RXN #2: $2H^+ + 2e^- \rightarrow H_2$

Cd plating is not 100% efficient –
some hydrogen also forms at the cathode during plating.

Preventing IHE

- **Cd plating is made porous (Treatment B) to allow hydrogen to escape during high temperature bake**
  - Dull Cd is required for HSS parts

Bake steel at 400° F for 24 hours to remove hydrogen from steel



Porous Cd still has good **<u>general</u>** corrosion resistance and is comparable to Bright Cd.
Microscopic porosity does not affect corrosion resistance.

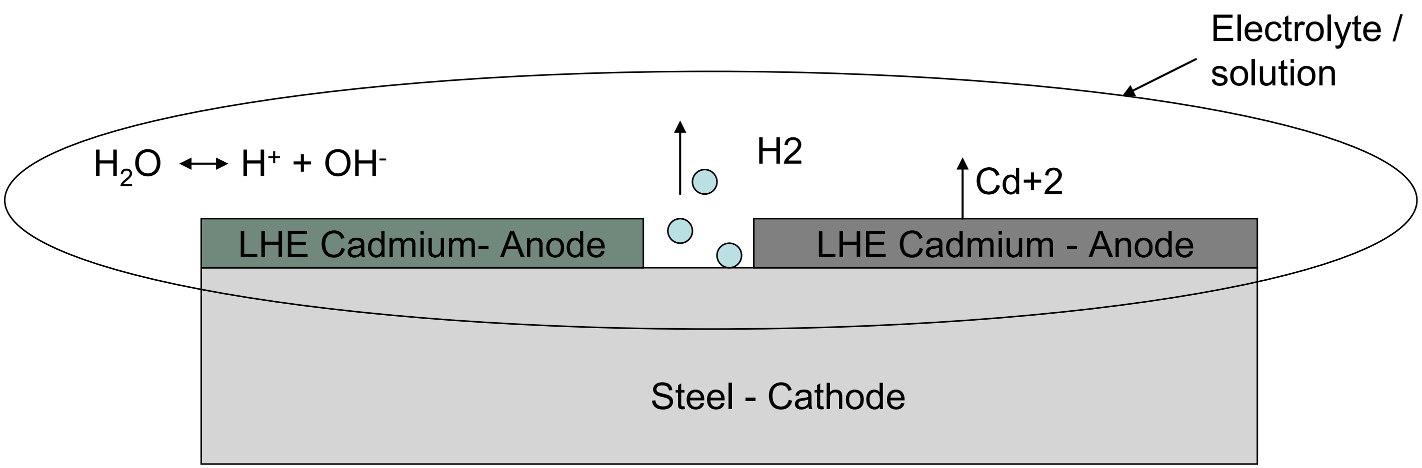
Testing for IHE

- **Cd Plate 4 ea ASTM F 519 Type 1a Test Specimens**
  - Visually inspect notch to verify that Cd plating is present – Cross-section to verify complete coverage
- **Bake test specimens within 4 hours of plating (375^{o} F x 24 hrs)**
- **Load Specimens at 75% NFS for 200 Hrs**
- **If Specimens Don't Break in 200 hours – Plating Process is Non-Embrittling**

Cadmium Plated Type 1a.1 Notch

EHE (Re-Embrittlement) of Cadmium Plate

- **What happens when Cd plated high strength steel comes in contact with environment?**
  - Natural Environment
    - Rain Water, Sea Water
  - Service Environment
    - Maintenance Fluids (Cleaners, Deicers, Paint Strippers, . . .)

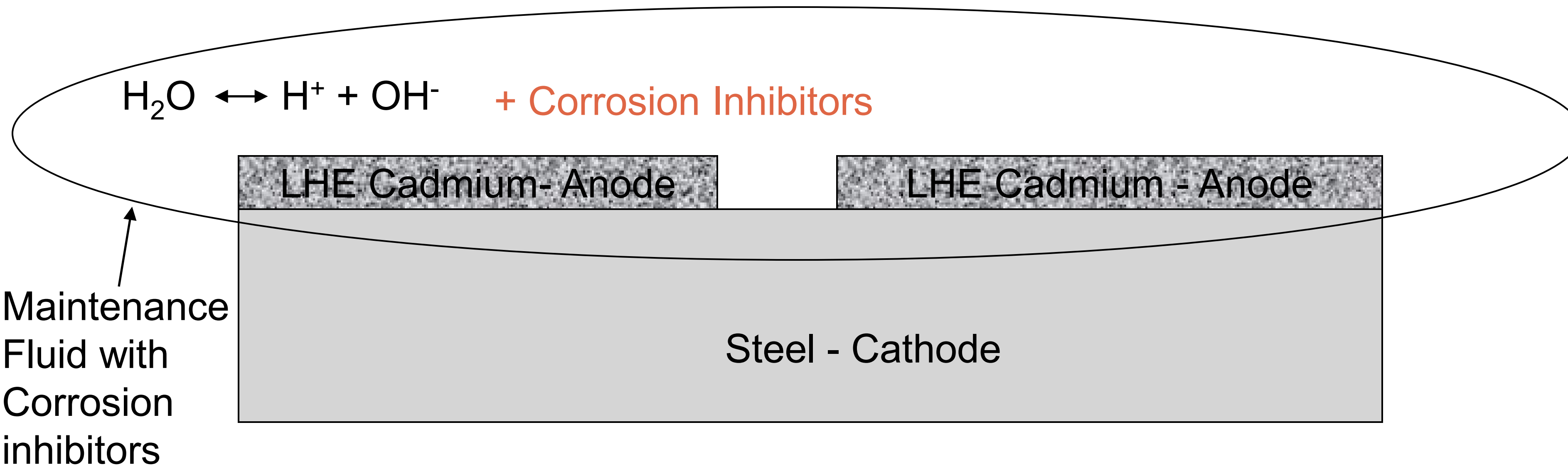


Porous Cd creates microscopic voids or thin areas that allow solutions (electrolyte) to come in contact with steel surface.

Anode RXN at Cd: $Cd \rightarrow Cd^{+2} + 2e^-$ Cathode RXN at Steel: $2H^+ + 2e^- \rightarrow H_2$

Preventing EHE (Service Environment)

- **Porosity of Cadmium Cannot Be Removed**
  - This would cause an increase in IHE failures
- **Adding corrosion inhibitors to maintenance chemicals will prevent EHE from occurring**



Stopping cathode reaction with corrosion inhibitors will prevent EHE of Steel.

No Cathode RXN at Steel: $2H^+ \rightarrow$ **NO HYDROGEN**

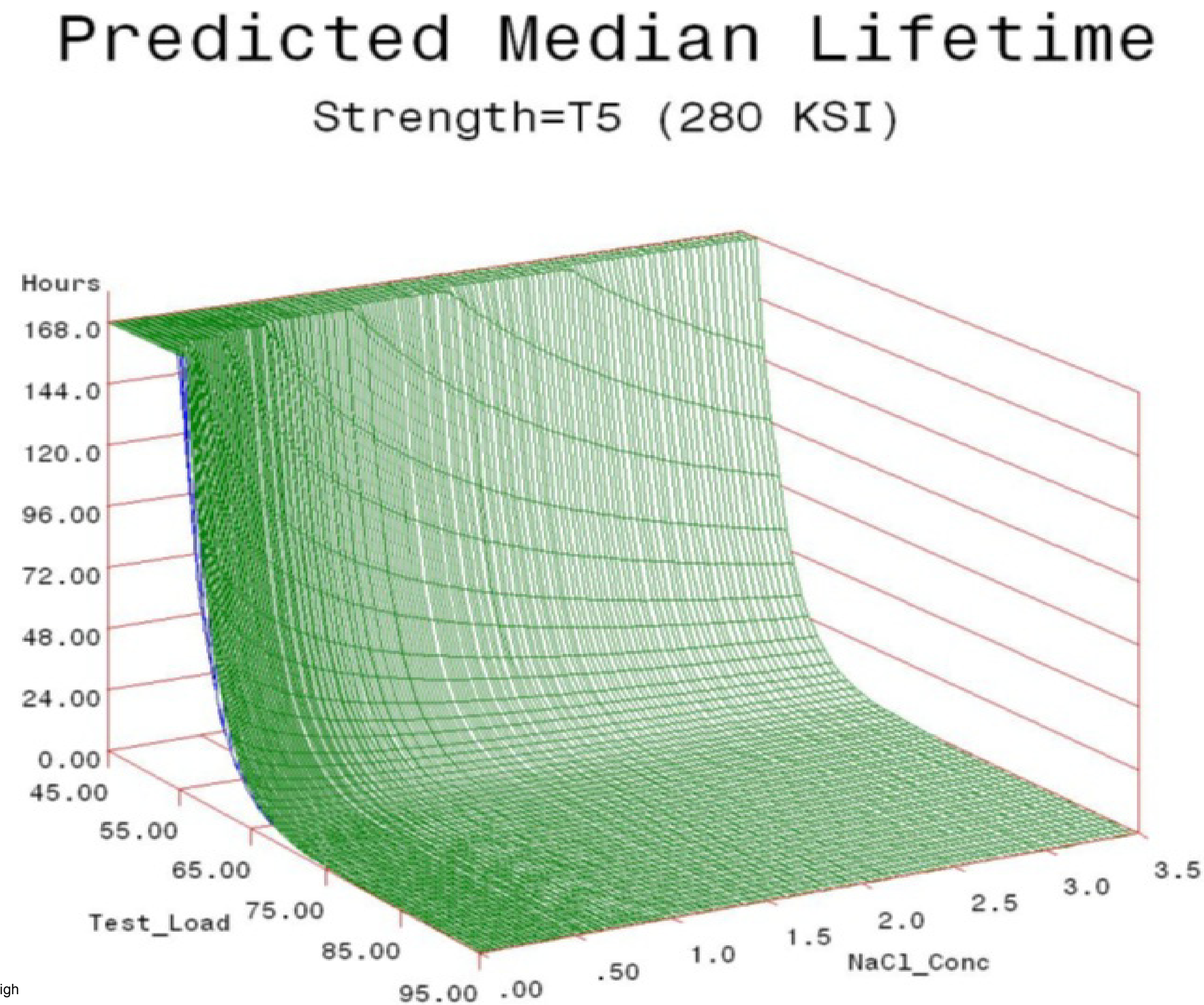
Testing for EHE (Re-Embrittlement)

- **1977 – Work carried-out by subcommittee F07.04 to develop a re-embrittlement test for ASTM F 519**
  - Round Robin testing conducted by Lockheed, Douglas and Boeing aircraft companies.
  - Water used as control to determine test conditions for qualifying maintenance fluids
  - 45% NFS for 150 hours was established as a test criteria for maintenance fluids
    - LHE Cd Plated Type 1a.2 at 45% NFS will fail this test when exposed to water
      - 3.5% salt water not tested but should be worse than water
  - Cd Plated Steel and Water used as criteria to develop re-embrittlement test in ASTM F 519, Annex A5
    - Used by numerous AMS and Mil Specs to qualify maintenance chemicals for use on aircraft

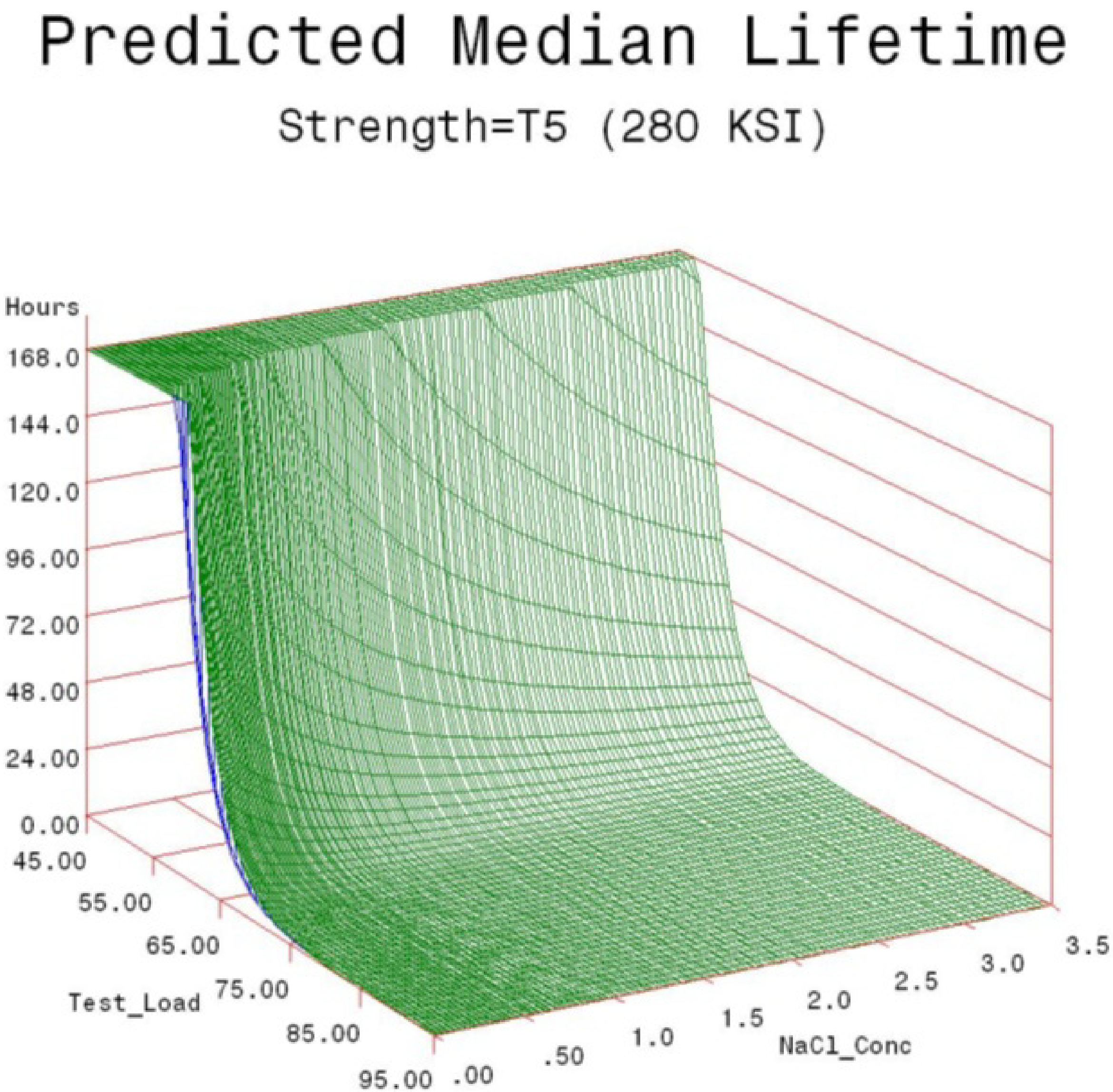
SERDP Hydrogen Embrittlment Project

- **Technical Objectives**
  - **Increase the implementation and utilization of environmentally friendly maintenance chemicals and cadmium alternatives by alleviating the HE obstacle.**
    - Year 1 – Life models for aerospace grade 4340 steel
    - Year 2 – Life models for prospective maintenance chemicals
    - Year 3 – Life models for prospective alternative coatings

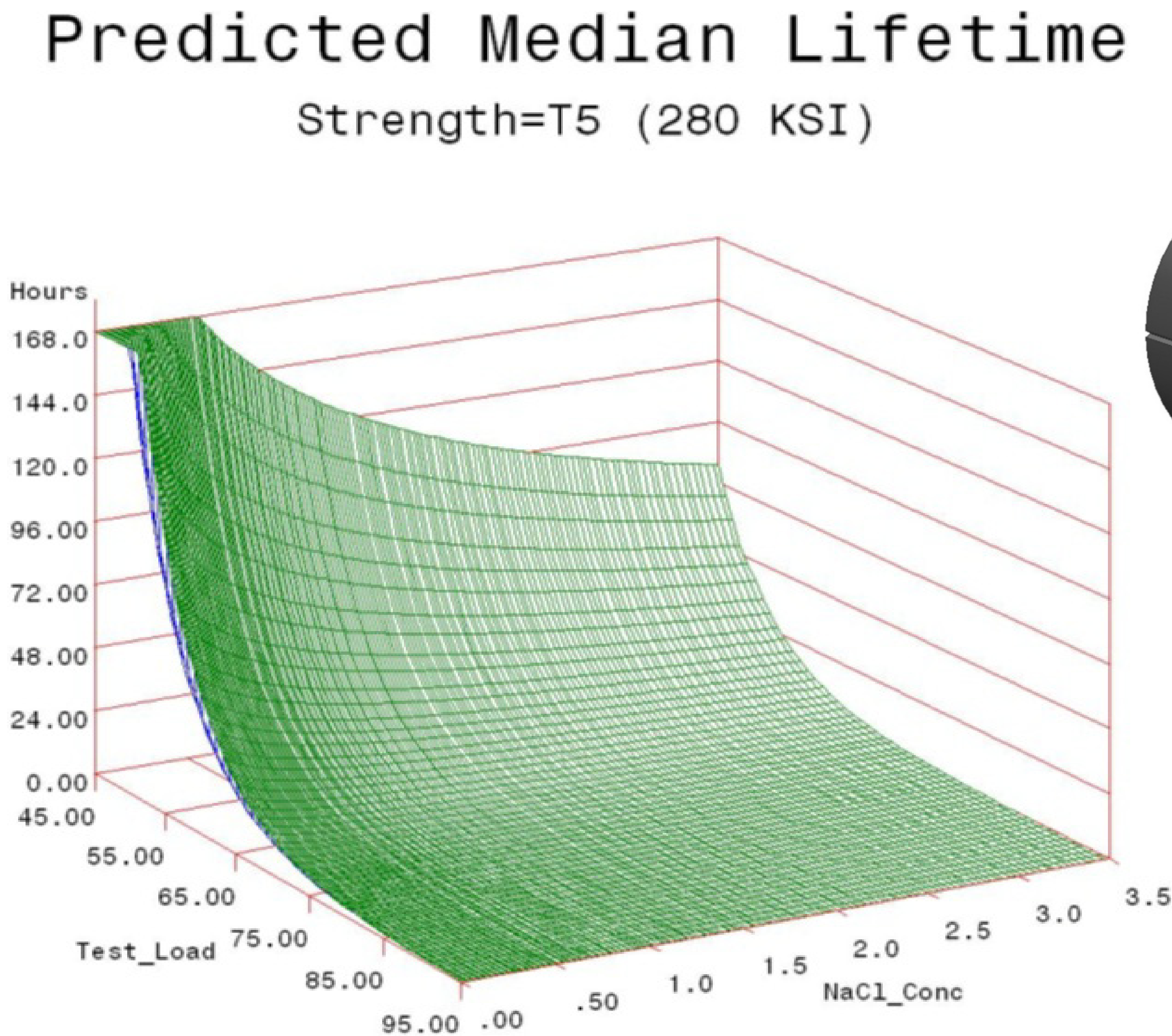
Type 1a.1 Results



Type 1a.2 Results



Type 1d Results



Cadmium IHE vs. EHE Conclusions

- **Porous Cd is applied to high strength steel and the porosity allows hydrogen to escape during baking - prevents IHE**
- **Cd sacrificially corrodes to prevent steel from corroding and hydrogen gas forms on steel when Cd is corroding to protect the steel**
  - Cadmium causes EHE of steel – not the environment
- **EHE can occur on HSS when porous Cd is used and fluids do not contain sufficient corrosion inhibitors to stop galvanic corrosion**
  - Insufficient coating of LHE Cd in notch increases occurrence of EHE
- **Porous Cd is used to prevent IHE but porous Cd does not help prevent EHE**
- **ASTM F 519, Annex A5 was developed to qualify maintenance chemicals and should only be used to qualify maintenance chemicals**

1977 - Search for Cadmium Alternatives

EPA-560/2-79-003

PROCEEDINGS OF THE

WORKSHOP ON ALTERNATIVES FOR CADMIUM ELECTROPLATING

IN METAL FINISHING,

October 4-6, 1977

Sponsored by:

Consumer Product Safety Commission
U.S. Department of Commerce
U.S. Department of Defense
U.S. Department of Health, Education, and Welfare
U.S. Department of the Interior
U.S. Department of Labor
Environmental Protection Agency
General Services Administration

at the

National Bureau of Standards
Gaithersburg, Maryland

Ion Implantation – Alternative to Cd?

Alternative Materials and Processes

Session I

Tuesday Morning 10:45

SURFACE ALLOYING BY ION IMPLANTATION:
AN ALTERNATIVE TO CADMIUM ELECTROPLATING

B. D. Sartwell
F. X. McCawley
College Park Metallurgy Research Center
Bureau of Mines, U.S. Department of the Interior
College Park, Maryland 20740

Abstract

The Bureau of Mines has fabricated a new class of alloys by implantation of low-energy metal ions into the surface regions of iron to doses ranging from 1.0 to 4.0 x 10^{16} ions/cm^2. The alloy distribution as a function of depth (depth profile) has been determined for polycrystalline iron samples implanted with either 25-keV chromium or nickel ions, and the results have been compared with theoretical predictions. The resistance of these "surface alloys" to environmental attack has been evaluated both by determining their anodic polarization behavior under potentiostatic conditions and by determining their gaseous oxidation characteristics. Results of the electrochemical studies have shown that the general corrosion resistances of the surface alloys were comparable to those of nominally equivalent bulk alloys and that the pitting-corrosion resistances for the surface alloys were superior to that for iron, although generally not as good as those for most equivalent bulk alloys. Gaseous oxidation studies have shown that surface and bulk iron-chromium alloys exhibit essentially identical oxidation kinetics, with a much higher rate of oxidation observed for iron. In both the aqueous corrosion and gaseous oxidation studies, the quantity of the alloying element used to fabricate the surface alloys was six to seven orders of magnitude less than that required to fabricate equivalent bulk alloys.

One of the principal disadvantages of surface alloying by ion implantation is that it is a "line-of- sight" process. Only surfaces that are directly exposed to the incident ion beam can be alloyed. Another

IVD Aluminum – Alternative to Cadmium

Alternative Materials and Processes

Session I

Tuesday Morning 12:10

ION VAPOR DEPOSITED ALUMINUM COATINGS

E. R. Fannin
McDonnell Aircraft Company
St. Louis, Missouri 63166

A process for the application of dense, uniform, and very adherent aluminum coatings has achieved production status. The process is a vacuum coating process and is referred to as ion vapor deposition (IVD). It can be used to replace cadmium coatings almost exclusively. Aluminum coatings can be used at temperatures up to 925°F, whereas cadmium is limited to 450°F. The IVD process can be used to coat high strength steel without fear of hydrogen embrittlement. It can also be used in contact with titanium without causing solid metal embrittlement. Cadmium is prohibited for this application. Finally, ion vapor deposition is a clean process and does not contribute to any ecology problems.

Details of the ion vapor deposition process, performance data, and current production applications at McDonnell Aircraft Company on both Navy and Air Force Programs will be discussed.

Zinc-Nickel Plating – Alternative to Cd

ELECTRODEPOSITION OF ZINC-NICKEL ALLOY COATINGS*

J. W. Dini
H. R. Johnson
Metallurgy and Electroplating Division 8312
Sandia Laboratories
Livermore, California 94550

ABSTRACT

One possible substitute for cadmium in some applications is a zinc-nickel alloy deposit. Previous work by others showed that electrodeposited zinc-nickel coatings containing about 85% zinc and 15% nickel provided noticeably better corrosion resistance than pure zinc. Present work supports this finding and also shows that the corrosion resistance of the alloy deposit compares favorably with cadmium.

2011 – Alternatives to Cadmium

- **Aluminum**
  - IVD – Only Coats OD Surfaces
  - Sputter – Developed to Coat ID Surfaces
  - Alumiplate
    - Supplier base issues
  - Ionic Liquid
    - R&D Stage
  - Cold Spray
    - Can be Used for Touch-Up and Repair
- **Alkaline Zinc-Nickel Electroplating**
  - Low Strength Steels – AMS 2417 (6 to 20% Ni)
  - High Strength Steels - LHE Zn-Ni (High Ni Content – No Brighteners)
    - AF Drawing 201027456 - Dipsol IZ-C17+
    - BAC5680 - Atotech ZNA
- **Stainless Steel, Titanium, Inconel**

Why Are IVD Al Coatings So Good?

- **Aluminum is non-toxic**
- **Provides Corrosion Protection to Steel**
- **Soft and Ductile and Does Not Reduce the Fatigue Life of High Strength Steel (HSS)**
- **Corrosion Resistant Coating in Salt Water and SO_2 Salt Spray (Compared to Zinc and Cd)**
- **Sacrificially Protects Steel in Salt Water**
- **Can be used at temperatures up to 925° F on HSS**
  - Does not Cause Liquid / Solid Metal Embrittlement of HSS
- **Can be used in fuel tanks**
  - Does not react with Fuel
- **Can be used next to Ti**
  - Does not embrittle Ti
- **IVD Al coating process is non-embrittling to HSS**

IVD Al Issues

- **IVD Al Process is Line of Sight only**
  - Cannot coat ID surfaces (inside of tubes)
- **IVD Al process is expensive and difficult to maintain**
  - Limited number of IVD Coating Suppliers
- **Aluminum coatings require lubricant on threaded fasteners**
- **IVD Al is Porous (Columnar – Dendritic Structure)**
  - Porosity causes poor performance in re-embrittlement (EHE) tests
    - Glass bead burnishing does not densify coating enough to affect re-embrittlement test results
  - Porosity does not affect corrosion performance
  - No reports from field on EHE failures for IVD Al coated parts

Why Are LHE Zn-Ni Coatings So Good?

- **Zn-Ni plating process is less toxic than Cd plating process**
  - Drop-in replacement process – minimum impact to supplier base
- **Provides Corrosion Protection to Steel**
  - Using TriCr CC or HexCr CC
- **Harder coating is more scratch and abrasion resistant than Cd**
- **Does Not Reduce the Fatigue Life of High Strength Steel**
- **Corrosion Resistant Coating in Salt Water (Better than Zn, Cd, Al)**
- **Sacrificially Protects Steel**
- **Can be used at temperatures > 450° F on HSS**
  - Does not Cause Liquid / Solid Metal Embrittlement of HSS
- **Zn-Ni plating process with embrittlement relief bake is non-embrittling to HSS**

LHE Zn-Ni Issues

- **Contains Ni**
  - Potential REACH issues
- **Requires lubricant on threaded fasteners**
- **Poor corrosion performance in SO2 salt spray (acidified)** – Similar to Cd
- **Causes Hydrogen Embrittlement Problems of HSS if not Properly Controlled** - Similar to LHE Cd
  - Controlled by Plating Methods and Baking Plated Parts
  - IHE and EHE Issues Similar to Cadmium
    - Porous LHE Zn-Ni needed to prevent IHE but porous Zn-Ni does not help prevent EHE

Conclusions

- **LHE Zn-Ni Plating is a good alternative to LHE Cd Plating**
  - Drop-in replacement
    - LHE Zn-Ni plating process safer to use than LHE Cd
      - LHE Zn-Ni eliminates Cd, Cyanides, and Cr^{+6} Process Tanks
  - Tri Cr CC or Hex Cr CC Can be Used on LHE Zn-Ni
    - Tri Cr CC Can Be applied before embrittlement relief bake
  - HE Performance of LHE Zn-Ni is similar to LHE Cd
    - LHE Zn-Ni Electroplating Process is non-embrittling
      - Tests show that 1 hour bake at 375° F is sufficient remove hydrogen
    - EHE issues with LHE Zn-Ni are similar to LHE Cd
  - Corrosion, Adhesion, and Fatigue Tests of LHE Zn-Ni or as good as or better than LHE Cd
    - However it appears that each program will run their own fatigue tests
- **Aluminum coatings are also good alternatives to Cadmium**
  - Just need to find a better way to apply aluminum to aircraft parts